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# SCIENCE

FRIDAY, NOVEMBER 1, 1912

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## THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

### SOME CHEMICAL RELATIONS OF PLANT AND SOIL<sup>1</sup>

IN order to arrive at a satisfactory theory of living matter it is evidently necessary to know what substances are indispensable to metabolism and to ascertain the rôle of each of these substances.

Despite much study it is not yet clear what constituents of the soil are absolutely needful for plants. An excellent example is found in sodium chloride, which is indispensable for animals, but is generally thought to be unnecessary for plants. This difference between plants and animals would be of fundamental importance if true in all cases, but recent experiments have shown that sodium chloride is just as necessary for many marine plants as it is for animals. It would not be surprising to find cases where sodium or chlorine are likewise necessary for land plants.

The condition in which the necessary substances exist in the soil has both practical and theoretical importance. In certain forms they are said to be "available" to the plant, in others not. A convenient method of determining quantitatively the substances which are "available" in a soil is one of the prime needs of practical soil study. In view of the difficulties with existing methods it would seem worth while to try to separate the available salts from the soil by means of an electric current.

<sup>1</sup> An address delivered at the Symposium on the Soil before Section G, American Association for the Advancement of Science, at Washington, 1911, the scope being limited to a brief presentation of elementary principles.

The chief process by which plant food becomes "available" is weathering, in which water and carbon dioxide play the chief rôles. The plant's supply of mineral salts as well as of carbon thus depends on the supply of carbon dioxide. The amount of this substance in the air is kept relatively constant not only by the production of carbon dioxide on the earth's surface, but by large amounts constantly escaping from its interior: and the ocean acts as a reservoir of carbon dioxide and a regulator of the amount in the air.

While the action of carbonic and other dilute acids benefits the plant by making plant food available, higher concentrations of acid may be injurious. As is well known, the acidity of the soil is a large factor in productiveness and some plants prefer acid soils while others show the opposite tendency. We are now in possession of a series of indicators which make it possible to ascertain various degrees of acidity found in soils without the labor of gas chain determinations, and these indicators may be used in the field.

An analysis of the factors of soil acidity is difficult on account of the many complications involved. Much aid may be expected from the application and extension of such careful quantitative studies as have recently been made on the ability of certain substances in solution to preserve the neutrality of the solution despite the addition of a considerable amount of acid or alkali to it.

To what extent the plant itself renders substances "available" by excretions from its roots is an unsolved problem. While it is generally agreed that the carbon dioxide excreted by the root is of importance in this respect, it is not certain whether other substances given out by the plant have a similar action. Investigation should be directed to the fatty acids which have been

said by various observers to be excreted by the root. It is important to determine whether these substances are given off by the living or by the dead cells.

There can be no doubt that the bacteria of the soil help to render mineral food available by producing carbon dioxide. According to recent investigations the bacteria in one hectare of soil to the depth of 40 cm. produce yearly several million liters of carbon dioxide. Hence it becomes important in judging the fertility of a soil to test the amount of carbon dioxide which it produces under natural conditions.

The supply of available mineral salts is commonly augmented by the application of mineral fertilizers upon the theory that a deficiency in the supply of any necessary substance constitutes a "limiting factor" which retards the development of the crop. The addition of the deficient substance produces a great increase in the crop: the relation between this increase and the amount of salt added has been expressed by Mitscherlich in a simple formula having a constant which is independent of the yield. The constant for any given salt is called its efficiency value.

It is not my province to discuss this subject further and I will only mention that the application of one substance may set free a different one; for example, where magnesium is applied to the surface of the soil the roots at a lower level may receive, not magnesium, but calcium in soluble form (Hilgard). Sodium has been used in this way to set free potassium. Further study of this subject will doubtless bring to light facts of importance.

Some of the substances thus set free may exist in a loose combination to which the term adsorption has been applied. But it is clear that a variety of processes are included under this term. In the first place there are reversible processes, as when a

dye is taken up by filter paper and is then completely washed out again by water. The rational formula which has been developed by Arrhenius for this process merits mention here.

Another process commonly called adsorption involves chemical change. An example is seen in the taking up of fuchsin from a watery solution by carbon: the fuchsin can not be washed off again by water, but is readily removed by alcohol. In this case the dye has been changed from a substance soluble in water to one insoluble in water but soluble in alcohol, which indicates the formation of an isomeric substance.

In other cases we may obtain the characteristic adsorption curve and yet be able to explain the phenomenon as a chemical reaction which involves no adsorption.

Numerous reactions take place in the soil which give the adsorption curve. The most important adsorbing substances are colloidal materials. Although colloids play a very important rôle in the soil, the rapidly accumulating discoveries in the field of colloidal phenomena have as yet found little application in soil studies. The use of the ultra microscope and of ultra filters capable of sorting out various grades of particles too small to be seen with the microscope, as well as the methods for measuring the rate of diffusion, the osmotic pressure, the viscosity and electrical properties of colloids, should find a place in the study of soil colloids. And we may expect important results from the application of the principles derived from the study of gel formation, of hysteresis, of the analogues of the Danysz effect, of temperature coefficients, of reaction velocity and similar fundamental matters which have proved fertile in the study of colloids. To speak of these in detail would take too much time. I will therefore mention only one.

According to the Gibbs-Thompson law substances which lower the surface tension tend to become more concentrated in the surface and reactions which produce such substances are favored at the surface. In the soil we deal almost entirely with surfaces, and it will be seen that the operation of this principle must promote such processes as oxidation and reduction where they tend to reduce surface tension and to retard them in the opposite case.

In the production of colloidal substances the organic materials in the soil play an important part. The great value of these substances is shown by the fact that good soil can be made without sand or clay but not without humus: fresh volcanic ash, consisting of finely ground minerals capable of furnishing plant food, must nevertheless await the admixture of humus before it can support crops.

Organic substances may combine chemically or mechanically with plant food and thus prevent it from being leached out of the soil.

Certain organic colloids are known to have a remarkable power of keeping difficultly soluble salts in solution at concentrations far above those which are possible in pure water. This consideration may prove important in soil studies.

The study of the organic substances in the soil is in a very backward state. It is known that some are beneficial and others are toxic and that in some cases the toxicity is partly removed by simple oxidation.

This leads us naturally to a consideration of oxidation in the soil. It is a striking fact that while some plants take up unoxidized substances and gain the energy they need by oxidizing them the majority of plants must have their food in a highly oxidized form in order to make the best use of it. Thus  $\text{CO}_2$  is a food while CO

is a poison: sulphates or nitrates are as a rule much better for the plant than the corresponding sulphites or nitrites. Most of the energy obtainable by oxidation of the latter substances is not available to the plant.

Thorough oxidation of the soil is one of the principal benefits of tillage and is a prime requisite for soil fertility: wherever it is interfered with by excess of water disastrous results follow, as may be seen in an extreme form in bogs. Investigations are being made on the oxygen content of bog waters and it is to be hoped that they may be extended to soil waters generally. Quantitative methods of estimating the rate of oxidation in soils under natural conditions are much to be desired.

The excretion of oxidizing and reducing catalyzers by living roots has recently been described and the statement has been made that the ability to oxidize such substances as gum guaiac (and to decompose hydrogen peroxide) is characteristic of good soil.

The study of catalyzers in the soil is a field in which we should have long since made a serious beginning. As I have just spoken of oxidation, an example from that field may be chosen to illustrate the point. It is well known that certain salts of manganese act as catalyzers which enormously increase oxidation, so much so that the minute traces of manganese which dissolve out from the glass vessels used in the experiment may affect the result. It is therefore possible that salts of manganese in the soil may affect fertility, and we may suppose that salts of iron and other substances may act in a similar way.

Another important field of study is found in the relation between those ions which are selected by the plant and those which it leaves in the solution. When the plant takes the K from a solution and leaves the Cl behind we have an illus-

tration of this. The separation of positive from negative ions in this manner results in electric stresses which tend to bring the processes to a standstill. This may be overcome in two ways: first, the plant may give up to the solution some other positive ion in place of the K it takes in. It is evident that if such a process is taking place our usual view of the process of absorption neglects one of the most important factors of the process, and thus we should speak of an exchange rather than of absorption of ions.

On the other hand, we may find that along with every K ion the plant absorbs an OH ion derived from hydrolytic decomposition. If the plant should take the  $\text{NO}_3$  ion and leave the Na we might find that along with every  $\text{NO}_3$  ion the plant absorbed an H ion produced by hydrolytic decomposition. This amounts to saying that in all cases when the plant selects one ion and leaves the other it takes up the absorbed substance in the form of a very dilute acid or alkali. It is hoped that some investigations which are now going on may throw some light on this subject.

A further question concerns the manner in which ions which have been absorbed by the protoplasm are prevented from diffusing out again. It seems necessary to assume that only those ions which unite into undissociable compounds can be retained in the protoplasm. In this way we may explain how potassium, which presumably forms such compounds, may accumulate in the plant to a greater extent than sodium.

It may be pointed out that the chemical effects of soil substances on the plant may be of at least four kinds:

1. *Toxic Action*.—A large number of substances found in soils are toxic in sufficiently high concentration. This is true of both organic and inorganic substances.

It should be borne in mind that a concentration far too weak to affect one organism injuriously may be toxic for another. Concentrations of sodium chloride which are too low to affect certain flowering plants may be quite toxic to certain algæ and *vice versa*.

The study of such relations, especially in the case of organic soil substances, is now being carried forward.

2. *Stimulatory Action*.—A considerable number of toxic substances (including such salts as sodium chloride) exert at certain concentrations a stimulating effect on metabolism. It is quite possible that this belongs to the same category as the catalytic action of enzymes and of mineral salts. It also seems quite probable that the stimulating substances often play the rôle of kinases. How this may come about is illustrated by the germination of the castor bean. In this case it is necessary that the fat stored in the seed be split up by the action of an enzyme (lipase) but this can not act rapidly except in the presence of an acid (kinase). The rôle of the acid appears to be to cause the enzyme to swell and emulsify. The castor bean produces sufficient acid for this purpose, but it is clear that in other cases the kinase may be absorbed from without and may sometimes be furnished by another organism. There is reason to suppose that kinases include a great variety of substances, both organic and inorganic.

It is quite possible that stimulating substances may act in other ways, as, for example, by altering the permeability of the protoplasm.

3. *Nutrient Action*.—As was said in the beginning, we are not yet sure in all cases what nutrient substances are needed nor what their rôle is in the plant. To take but a single example we may select calcium. So important is it that we find plants classified ecologically into those

which prefer lime soils and those which avoid them. A high authority very graphically describes how in the Mississippi Valley, in passing a region rich in lime to one where it is less abundant, the appearance of the trees changes: from being densely branched with thick foliage they become sparsely branched, so much so that the former region is avoided by squirrel hunters because the game can too easily hide in the dense tree tops. The crops become less and less, while barns and houses grow smaller as the soil grows poorer in lime.

Various hypotheses have been advanced to explain the effects of calcium. It was supposed to play an essential part in photosynthesis, but it appears that some of the lower green algæ may carry on photosynthesis in complete absence of calcium.

It was also supposed to form (in combination with proteid) an indispensable part of the nucleus, but many fungi and some of the algæ thrive without it, despite the fact that their nuclei and mitotic processes are apparently similar to those of plants which require calcium.

A more satisfactory view of this question is possible from the standpoint of protective action.

4. *Protective Action*.—It is well known that many toxic effects may be overcome more or less completely by the addition of other substances. When one substance thus acts as an antidote to another it is said to have a protective action. It is by no means necessary that the protective substance should itself be toxic, though it frequently is so; nor is it necessary that it should have any nutritive value. A large number of cases are now known in which mineral salts act as more or less efficient antidotes to other salts or to organic substances.

If we apply these principles to the case we have just now discussed, namely, the

rôle of calcium, we shall see that they clear up many puzzles. As long as we try to explain all the benefits of lime merely as nutrient effects we can not account for its special importance. But as soon as we learn that lime is extraordinary in its *protective* action, which greatly surpasses that of all other substances in the soil, its importance becomes self-evident. This protective action is so great that a single calcium ion acts as an antidote to from 20 to 100 ions of sodium, potassium, ammonium, etc.

To make clear that this result may be quite apart from its nutritive action it may be mentioned that lime is unnecessary as a nutrient for many fungi, and the ordinary nutrient solutions for these plants are made up without it. But if the concentration of the nutrient solution be too high it becomes toxic: then the addition of lime overcomes this toxicity, without adding any nutrient, and makes an extraordinary increase in the growth of the plants.

The great importance of protective action has led to a number of attempts to explain how it is brought about. It was early suggested by Loeb that one salt may prevent the toxic action of another by preventing it from entering the cell. This suggestion has not been put to decisive experimental test until recently. The outcome is extremely satisfactory: it may be illustrated by the following typical case. *Spirogyra* placed in 0.1 M NaCl solution quickly died, but it lived a long time if a very small amount of  $\text{CaCl}_2$  was added (1 molecule of  $\text{CaCl}_2$  to each 100 molecules of NaCl). In order to find out whether the calcium hindered the sodium from entering the cell, the plants were placed in a solution of NaCl strong enough to produce plasmolysis. On observing them continuously under the microscope the cells were seen to recover from plasmolysis, the protoplasm expanding so as to com-

pletely fill the space inside the cell wall. This could only be interpreted as due to the penetration of NaCl, which thus raises the osmotic pressure within the cell. But if the *Spirogyra* be plasmolyzed in a solution of NaCl containing a little  $\text{CaCl}_2$  (1 molecule of  $\text{CaCl}_2$  to 100 molecules of NaCl) the recovery takes 10 hours instead of the half hour required when it is in pure NaCl. It is therefore obvious that the penetration of the NaCl is hindered by the presence of  $\text{CaCl}_2$ .

The same thing is shown by experiments on *Laminaria*, in which the rate of penetration of the ions of NaCl is directly measured by electrical means. Here the addition of a very little  $\text{CaCl}_2$  hinders the penetration of the ions of NaCl in the most striking way.

It may be asked how merely delaying the entrance of a salt produces a beneficial effect. It is a well-known phenomenon that the sudden addition of a salt may produce precipitation of a colloid when the slow addition of the same amount produces no such effect. Similar facts are familiar in biology. Moreover, there is good evidence that when NaCl finally begins to penetrate the cell in a mixture of NaCl +  $\text{CaCl}_2$  the  $\text{CaCl}_2$  enters along with the NaCl; it may thus hinder the NaCl from entering various internal cell membranes (such as the nuclear membrane). It may also have other effects on the protoplasm.

We may therefore conclude that the mechanism of antagonism consists primarily in hindering the penetration of toxic substances, just as calcium hinders sodium from entering the cell. That the calcium does this by directly affecting the plasma membrane is shown by a variety of evidence which can not be described here.

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